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# THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION

# FORMATION, STABILITY AND CRYSTAL STRUCTURE OF SOLID SILICON MONOXIDE

by

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Technical Report

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# FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under contract with U.S. Navy, Office of Naval Research Contract Number N6ori-17, Task Order IV, ONR Project Number NR 058 039, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: "High Temperature Thermodynamics of Inorganic Substances." It represents the 7th Technical Report of this series.

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## ABSTRACT

The formation of solid silicon monoxide from a mixture of silicon and silicon dioxide according to the reaction $Si + SiO_2 \longrightarrow 2SiO$ was observed from x-ray diffraction patterns taken at 1250° and 1300° C, during various time intervals. At 1250° C no SiO is formed. At 1300° C the mixture of Si and $SiO_2$ was completely transformed into SiO, after about nine hours of heating. The three x-ray diffraction patterns taken during this nine-hour period show a decrease in intensity of the Si diffraction lines and the appearance of a new set of diffraction lines, corresponding to those of SiO, whose intensities increased during this period.

The $SiO_2$ used was amorphous and did not crystallize even after prolonged heating. Since SiO, on slow cooling, disproportionates back to Si and $SiO_2$, the SiO was rapidly quenched (from 1300° to 850° C in 2 sec), thereby resulting in a mixture of $SiO_2$, SiO and Si. This procedure enabled us to obtain a diffraction pattern of SiO at 25° C.

The crystal structure and lattice constants of Si and SiO were determined at 1300° and 25° C. Results showed that Si has the same body-centered lattice at 1300° C as at room temperature, with a lattice constant of a = 5.445 Å at 1300° C and a = 5.413 Å at 25° C. The lattice of SiO was found to be cubic, the lattice constants at 1300° and 25° C being 7.135 Å and 7.09 Å, respectively.


## INTRODUCTION

The existence of SiO has been proved by Bonhoeffer (1) from measurements of the adsorption spectrum. Since then several attempts have been made to obtain solid SiO, but without success. Silicon dioxide was heated in vacuum to 1100°-1500° C in the presence of a reducing agent (mostly Si or C), and high rate of evaporation was observed (2, 3, 4, 5, 6). The substances which condensed on

the cold walls of the tube were amorphous and the faint x-ray diffraction lines indicated the presence of silicon and Crystoballite (7). Very faint and unconvincing electron diffraction patterns of the distillate were obtained by H. de Wet Erasmus, and J.A. Persson (8). A description of the reactions of the distillation product is presented in a paper by Zintl (2). Grube and Speidel (3) measured the vapor pressure of SiO from the reaction $SiO_2 + H_2 \rightarrow SiO + H_2O$, and Geld and Kochnev (6) measured the vapor pressure of this substance at temperatures between $900^\circ$-$1155^\circ$ C.

Schaefer and Hoernle (9) measured the partial pressure of SiO over a mixture of Si and $SiO_2$ between $1050^\circ$ and $1200^\circ$ C. They concluded that at this temperature no solid SiO exists and that the mixture consists of only $SiO_2$ and Si.

The best method of observing the formation of SiO, according to the reaction $SiO_2 + Si \rightarrow 2SiO$ where only solid components are present, is to take x-ray diffraction pictures during the reaction. If the reaction is slow, as is the case for solid reactions, so that two or more x-ray diffraction patterns can be taken during the reaction, then the consecutive patterns show a decrease in intensity of the diffraction lines of the reactants and the appearance, with increasing intensity, of the diffraction lines of the products. It is, of course, necessary that the components do not undergo a change in crystal structure at the reaction temperature.

During the present investigation, the crystal structures of Si and $SiO_2$ were studied at $1300^\circ$ C. and then the reaction between Si and $SiO_2$ was followed at this temperature, using the method described above. The disappearance of the Si diffraction lines and the appearance of a new set of diffraction lines, besides the fact that upon cooling the sample to room temperature this new set of lines was found to disappear while the Si lines reappeared, constitute proof of the formation of solid SiO.

## MATERIALS AND EXPERIMENTAL PROCEDURE

The x-ray diffraction patterns were taken in our high temperature camera which has been described elsewhere (10) A few changes

were made in this apparatus in order to improve its performance. The high temperature patterns were taken under a pressure of helium of 800 mm to avoid evaporation of the sample. The temperature was measured with a Leeds and Northrup disappearing filament optical pyrometer which had been calibrated against a standard lamp obtained from the National Bureau of Standards. The temperature calibration of the camera was carried out by placing a "black body" made out of a piece of tantalum tube in place of the x-ray specimen. By taking account of the various calibration and correction factors, the uncertainty in the reading of the pyrometer, and the slight temperature variations during the runs, the temperature may be considered accurate to within 20°. Ni-filtered Cu $K_\alpha$ radiation, obtained from a Machlett tube operated at 50 Kv and 20 Ma, was used. The exposure time was three hours.

The silicon was in the form of a powder and was obtained from C. Hardy, Inc., New York; the $SiO_2$ was Baker analyzed and was in amorphous power form. Rods of 1/32" diameter were pressed from Si, $SiO_2$ and the Si + $SiO_2$ mixture and placed into the camera. After filling with helium, the camera was heated and the x-ray diffraction patterns were taken. When the pattern had been taken, the camera was cooled, a new film inserted, and the process was repeated.

## EXPERIMENTAL RESULTS

Silicon was found to have the same crystal structure at 1300° C as at room temperature. The lattice constant was determined, from the back reflection lines, to be $a = 5.445 \pm 0.002$ Å.

The $SiO_2$ was amorphous and heating it for twenty hours failed to crystallize it.

When heated to 1250° C, the mixture of Si and $SiO_2$ reacted only slightly, if at all, since only the Si diffraction pattern could be obtained. At 1300° C, the reaction took place slowly and was completed in about nine hours. Figure 1 shows the three patterns obtained during the reaction; pattern No. 1 still shows the Si diffraction lines, with very faint SiO lines; pattern No. 2 shows Si and SiO lines in about equal intensity; pattern No. 3 shows only SiO lines with faint Si diffraction lines. The diffraction lines of SiO were identified from pattern No. 3 and found to be cubic (see Table I). The lattice constant of SiO at 1300°, obtained from back reflection lines, is $a = 7.135 \pm 0.002$ Å.

TABLE I

X-RAY DIFFRACTION LINES OF SiO AT 1300° C

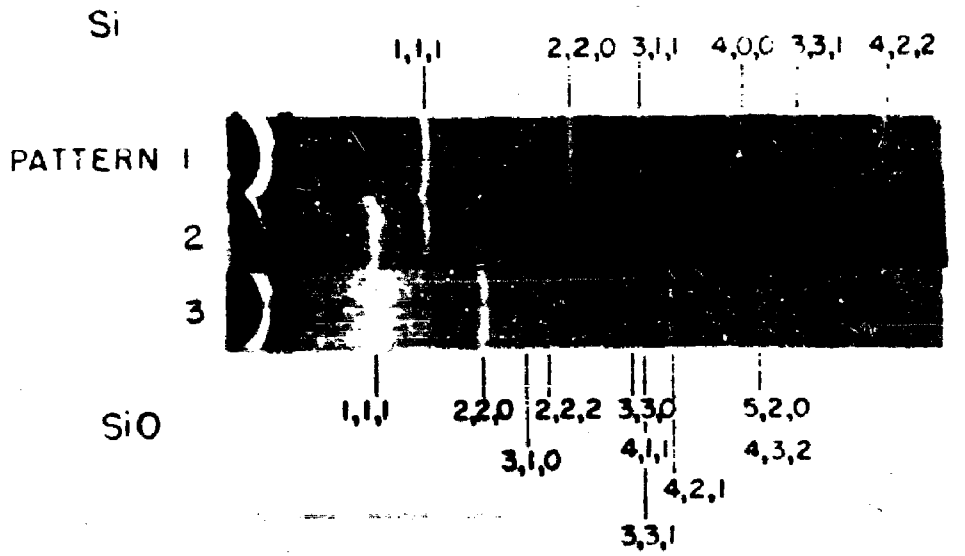
| Intensity | $\sin^2\theta$ | Indices h, k, l |
|---|---|---|
| Strong | 0.0348 | 1, 1, 1 |
| Strong | .0924 | 2, 2, 0 |
| Weak | .1238 | 3, 1, 0 |
| Weak | .1409 | 2, 2, 2 |
| Very weak | .2118 | 4, 1, 1 3, 3, 0 |
| Very weak | .2197 | 3, 3, 1 |
| Medium | .2477 | 4, 2, 1 |
| Medium | .3389 | 5, 2, 0 4, 3, 2 |
| Weak | .7429 | 8, 0, 0 |
| Weak | .8352 | 8, 2, 2 6, 6, 0 |

After pattern No. 3 of Figure 1 was taken the sample was rapidly quenched (from 1300° to 850° C in 2 sec) and an x-ray diffraction pattern at room temperature was obtained (shown in Figure 2). Besides the SiO diffraction lines, Si lines appear, due to some disproportionation into Si and $SiO_2$. The pattern shown in Figure 2 was used to determine the lattice constant of SiO at 25° C, the result being $a = 7.093 \pm 0.004$ Å.

An attempt was made to obtain a larger quantity of SiO at room temperature in the following way: A mixture of 4 g of Si and $SiO_2$ was heated to 1300° C for nine hours in a tantalum container, and then quenched. However, the obtainable quenching speed was too slow (from 1300° to 850° C in 10 sec) and the x-ray diffraction pattern of the powder contained strong Si diffraction lines and two faint SiO lines. The same results were obtained when the x-ray sample was heated to 1300° C, after taking the pattern of Figure 2, and then slowly cooled.

These measurements, therefore, have led to the following results: SiO is formed in the solid phase above 1250° C, has a cubic crystal structure with lattice constant of $a = 7.135$ Å at 1300° C, and disproportionates to Si and $SiO_2$ upon cooling.

FIG 1 X RAY DIFFRACTION PATTERNS TAKEN AT 1300°C
SHOWING THE REACTION $Si + SiO_2 \rightarrow 2\,SiO$



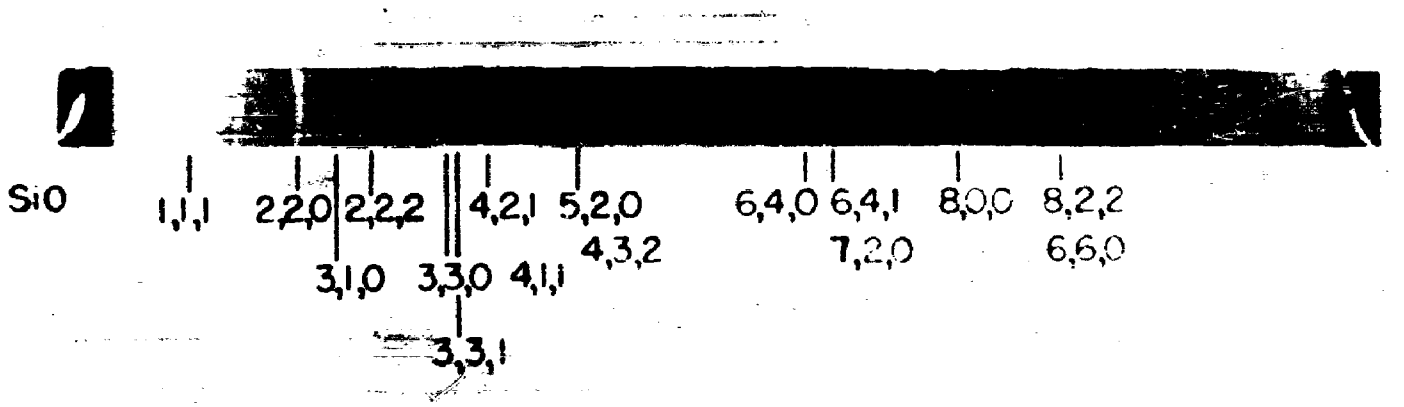




FIG. 2 X-RAY DIFFRACTION PATTERN TAKEN AT ROOM TEMPERATURE OF SiO QUENCHED RAPIDLY (1300° – 850°C IN 2 SEC)

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